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# Integral Equation Calculation of Solvent Activation Free Energies for Electron and Proton Transfer Reactions

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The extended reference interaction site method (RISM) integral equation theory is applied to calculate the solvent activation free energy for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  electron transfer and a model proton transfer reaction in water. In the case of the electron transfer, the calculated free energy is found to be within a few percent of an existing computer simulation result. In the case of the proton transfer reaction, the agreement with simulation is not as good, but still reasonable.

## I. Introduction

Electron and proton transfer reactions are among the most fundamental of chemical processes. The important role of the solvent activation in the electron transfer process was recognized by Marcus many years ago.<sup>1,2</sup> In particular, the concept of a solvent reaction coordinate and associated free energy functions have played an important role in many theoretical and experimental studies. These free energy functions were first calculated by Marcus using a continuum dielectric approach<sup>1,3</sup> and statistical mechanics<sup>4</sup> for electron transfer in homogeneous solutions,<sup>1</sup> for electron transfer at metal-liquid<sup>4,5</sup> interfaces, and later for semiconductor-liquid and liquid-liquid interfaces.<sup>6,7</sup> This perspective on the solvent participation in electron transfer was further developed by Levich<sup>8</sup> and Dogonadze.<sup>9</sup>

Free energy functions for electron transfer reactions have been studied extensively using Monte Carlo and molecular dynamics simulation techniques.<sup>10-15</sup> For example, Warshel and co-workers<sup>10</sup> have studied the behavior of the Marcus free energy curves, particularly in the "inverted" region. Kuharski *et al.*<sup>11</sup> performed extensive simulations on the  $Fe^{2+}/Fe^{3+}$  redox pair in water and provided conclusive evidence that Marcus behavior would be valid in realistic condensed phase systems. Carter and Hynes<sup>12</sup> also performed a molecular dynamics study and found larger curvature of the solvent free energy near an ion pair than near a neutral pair of atoms—an effect also investigated earlier by Kakitani and Mataga,<sup>13</sup> though both studies were called into question by Tachiya.<sup>13</sup> More recently, Benjamin<sup>14</sup> has calculated the free energy curves for electron transfer across the interface between two immiscible liquids, while Straus and Voth have done the same for the metal-water interface.<sup>15</sup>

In the field of proton transfer, the current understanding of the solvent participation in the reactive event again has its origin in the phenomenology for charge transfer developed by Marcus,<sup>1-7</sup> and others.<sup>8,9</sup> Computational efforts have focused on the calculation of the solvent contribution to the activation free energy,<sup>16-24</sup> studies of intramolecular effects arising from the modulation of the proton tunneling by molecular vibrations,<sup>21-23</sup> and simulations of adiabatic proton transfer in strongly hydrogen-bonded complexes.<sup>24</sup>

As opposed to simulations, integral equations have been employed to calculate solvent activation free energies for charge transfer reactions in only a few cases. Rossky

and co-workers<sup>25</sup> carried out extended Reference Interaction Site Model (RISM) integral equation<sup>26-30</sup> calculations to examine the aqueous phase  $S_N2$  reaction of a chloride ion with methyl chloride. This integral equation approach was particularly effective for efficiently examining the shape of the free energy surface, the variation of the results with changes in the solvent model, and the relative contribution of entropy to the net free energy. In the field of electron transfer, Kuharski and Chandler<sup>31</sup> have also applied the extended RISM method to study the solvation structure and thermodynamics of di- and tri-valent iron ions in aqueous solution. In other integral equation studies of electron transfer, analytical expressions for the Born solvation free energy of a pair of ions with arbitrary charges, unequal size, and fixed separation have been obtained via an interaction-site approach with the mean-spherical approximation (MSA).<sup>32</sup> In the latter study, the results for ions in a dumbbell solvent, in a dipolar hard-sphere solvent, and in an ionic solution in a dielectric continuum solvent were compared. The results from the theory for the  $Fe^{2+}/Fe^{3+}$  electron transfer were qualitatively compared with simulation results. Most recently, Fonseca *et al.*<sup>33a</sup> have calculated the solvent force constant which governs solvation free energy fluctuations via the reference hypernetted chain (RHNC) integral equation approach<sup>33b</sup> for ionic solutes in model dipolar-quadrupolar solvents.

It should be noted, however, that there are numerous challenges in using existing integral equation theories to calculate activation free energies for charge transfer reactions. For example, one difficulty is in the appropriate form of the closure relation. In integral equation theories, the closure enumerates the diagrams which depict the interactions. Out of all the relevant closures, the Percus-Yevick (PY) closure has proven most appropriate for hard-sphere systems. Thus, short range interactions are reasonably accounted for with the PY closure. By separating the bare potential into a long range and a short range contribution, the MSA closure corrects the PY closure for weak attractive or repulsive tails to a repulsive core, but this approach becomes less accurate for strongly interacting long range systems. For the latter kind of system, the HNC closure has proven to be quite useful in RISM theory. However, while the HNC closure does introduce dielectric screening into the RISM theory, the dielectric constant it predicts depends only on the intramolecular correlations defined by the correlation function  $\omega$ . The latter quantity is

independent of the intermolecular correlations and thereby RISM calculations may yield an inaccurate value for the dielectric constant.

Even though the application of integral equation theories to charge transfer reactions in polar solvents may be problematical, there is a strong intellectual and practical motivation to do so. With regards to the practical motivation, one needs only to consider the difficulties inherent in computer simulations of systems with strong long range forces. For example, Bader and Chandler<sup>34</sup> have used computer simulation methods to study the potential of mean force between two iron ions in a periodically replicated simple point charge model (SPC) of liquid water. Their numerical results were found to depend significantly on the treatment of the long range forces. Specifically, if the long range forces were truncated at half the simulation box length, the potential of mean force between the iron ions was found to be nonmonotonic, exhibiting an attraction at interionic distances beyond 6 Å. However, it was also found by Bader and Chandler that if Ewald sums were performed, the potential of mean force was monotonic and close to a screened Coulombic type of interaction.

In the present paper, the accuracy of the RISM method for calculating the solvent contribution to activation free energies in electron and proton transfer processes is explored. In the integral equation studies described in the following sections, the solvent system consists of the water molecules and comprises the most basic input for the theory, namely the solvent-solvent correlation functions. The solute-solute, solute-solvent and solvent-solvent interactions are used as accurate inputs (either obtained from simulations or analytically derived) for the appropriate (in this case HNC) closure. The solvent contribution to the excess free energy is then calculated. Since the ions are a perturbation on the pure solvent, the quantity being calculated, therefore, is the solvent's response to the ions and its corresponding reorganization. The difference in excess free energy of the entire solvent-solute system between its reactant state and the transition state is defined as the solvent activation free energy.

The following sections of this paper are organized as follows: In Section II, a brief review of the RISM equation is given. An application of the RISM theory to the model for the aqueous  $\text{Fe}^{3+}/\text{Fe}^{2+}$  electron transfer reaction is then given in Sec. III. Next, Sec. IV

contains an application of the RISM theory to a model aqueous proton transfer reaction which differs significantly from the electron transfer system. Concluding remarks are given in Sec. V.

## II. RISM Theory

### A. Formalism

The RISM integral equation,<sup>26-30</sup> in its extended form,<sup>35,36</sup> can be applied to liquid solutions with long range forces. For example, Pettitt and Rossky<sup>35</sup> have formulated and applied the extended RISM equation to several three-site models of water. In that study, the site-site correlation functions were calculated and compared to available computer simulation results. Furthermore, the variation of liquid state structure with the model-site charge was examined, and it was found that the integral equation approach provides a correct qualitative description of the liquid structure. Rossky and coworkers<sup>36-38</sup> have also provided considerable evidence that the extended RISM approach provides a reasonable alternative to computer simulations for the analysis of aqueous solutions and ionic solvation.

The explicit RISM equation<sup>26-30</sup> for a molecular fluid of molecular number density  $\rho$  is given by

$$\rho \mathbf{h}_{\alpha\gamma} \rho = \omega * \mathbf{c}_{\alpha\gamma} * \omega + \omega * \mathbf{c}_{\alpha\gamma} * \rho \mathbf{h}_{\alpha\gamma} \rho \quad (1)$$

where all matrices are site-site labeled;  $\alpha, \gamma$  being two distinct sites within the same species, or different species, as the case may be.  $\mathbf{h}$  is the matrix of intermolecular pair correlation functions,  $\mathbf{c}$  is the matrix of direct correlation functions,  $\rho$  is a diagonal matrix of site densities, and  $\omega$  is an intramolecular correlation function. The latter quantity is defined as

$$\omega_{\alpha M \gamma M'} = \rho_M \delta_{MM'} [\delta_{\alpha M \gamma M'} \delta(\mathbf{r}_{\alpha M} - \mathbf{r}_{\gamma M'}) + (1 - \delta_{\alpha M \gamma M'}) s_{\alpha M \gamma M'}(\mathbf{r}_{\alpha M} - \mathbf{r}_{\gamma M'})] \quad (2)$$

for site  $\alpha$  in molecule  $M$  and site  $\gamma$  in molecule  $M'$ . Here,  $\delta_{\alpha M \gamma M'}$  is the Kronecker delta,  $\delta(\mathbf{r})$  is a delta function, and  $s(\mathbf{r})$  is the intramolecular pair distribution function between

distinct sites in the same molecule. For rigid bonds, the latter function is taken to be a delta function in  $\mathbf{r}$  space. In the above notation, an analog of the HNC equation constitutes the closure relation and is written as

$$c_{\alpha\gamma} = -\beta u_{\alpha\gamma} + \phi_{\alpha\gamma} h_{\alpha\gamma} - \ln[1 + h_{\alpha\gamma}] \quad (3)$$

### B. Numerical Solution of the RISM equation

The set of RISM equations to be solved now will be discussed. As previous work has shown,<sup>36</sup> the correlation matrices can be considered site-ordered according to different classes of species. The species in the present case are the solvent or the solute. Equation (1) then separates into three equations for  $\mathbf{h}^{vv}$ ,  $\mathbf{h}^{uv}$ ,  $\mathbf{h}^{uu}$ , which are the solvent-solvent, solvent-solute and solute-solute correlation function matrices, respectively. The following set of coupled integral equations are then obtained:

$$\rho \mathbf{h}_{\alpha\gamma}^{vv} \rho = \omega * \mathbf{c}_{\alpha\gamma}^{vv} * \omega + \omega * \mathbf{c}_{\alpha\gamma}^{uv} * \rho \mathbf{h}_{\alpha\gamma}^{vv} \rho \quad (4)$$

$$\mathbf{h}_{\alpha\gamma}^{uv} \rho = \mathbf{c}_{\alpha\gamma}^{uv} * \omega + \mathbf{c}_{\alpha\gamma}^{uu} * \rho \mathbf{h}_{\alpha\gamma}^{vv} \rho \quad (5)$$

$$\mathbf{h}_{\alpha\gamma}^{uu} = \mathbf{c}_{\alpha\gamma}^{uu} + \omega * \mathbf{c}_{\alpha\gamma}^{uv} * \rho \mathbf{h}_{\alpha\gamma}^{vv} \quad (6)$$

where  $\rho$  refers only to the solvent (i.e., in the present applications, the density of the solute is entirely negligible compared to the solvent). In Eqs. (4), (5) and (6),  $\mathbf{h}_{\alpha\gamma}$  and  $\mathbf{c}_{\alpha\gamma}$  may be the solvent-solvent, solute-solvent, or solute-solute pair correlations. Since each site may carry a charge, it is most convenient to cast these equations in renormalized form and then use a closure which takes advantage of this renormalization. The details of this method was done by Rossky and co-workers in several of their papers.<sup>35,36,38-40</sup> With the closure relation in Eq. (3), one can solve for Eqs. (4), (5) and (6) sequentially. That is, first Eq.(4) is solved for the pure solvent-solvent correlations. After that, the solution of Eq.(4) is used as input for Eq.(5) and one solves for the total solvent-solute pair correlation functions. Next, the solution of Eq.(5) is used to get the total solute-solute pair correlation functions in Eq. (6).



The solvation free energy  $\mu_{solv}$  is obtained from the Singer-Chandler relationship.<sup>41</sup> It is the solvation contribution to the solute chemical potentials and is given by

$$-3\mu_{solv} = \rho \sum_{\alpha s} \int_{-\infty}^{\infty} d\mathbf{r} [c_{\alpha s}(r) - \frac{1}{2}h_{\alpha s}^2(r)] + \frac{1}{2(2\pi)^3} \sum_{\alpha, \gamma, s, s'} \int_{-\infty}^{\infty} d\mathbf{k} c_{\alpha s}(k) \chi_{ss'}(k) c_{s'\gamma}(k) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (7)$$

where  $\alpha$  and  $\gamma$  are indices for the solute while  $s$  and  $s'$  are indices for the sites of the solvent. The correlation function  $\chi_{ss'}$  in Eq. (7) is expressed within the context of the right-hand-side of Eq. (4) as  $\omega + \rho \mathbf{h}_{\alpha\gamma}^{uv} \rho$ . An alternative solvation free energy expression,<sup>42</sup> which can be derived from Gaussian field theory, is given by Eq. (7) but without the  $(1/2)h_{\alpha s}^2(r)$  term. The latter expression may give better results in some cases,<sup>43</sup> but it was not found to give substantially different results from Eq. (7) in the present work. From the last set of pair correlation functions in Eq. (6), one can also determine the potential of mean force between the two solute sites  $\alpha$  and  $\gamma$ , given by

$$\Omega_{\alpha\gamma} = -k_B T \ln(h_{\alpha\gamma}^{uu} + 1) \quad (8)$$

Equations (4)-(6) were all expressed as matrix convolution products in real space. The equations are iterative and were expanded through fifth order in the integrals themselves. While performing the calculations, the iterative equations were also expanded through seventh order. However, there was not much difference between the seventh order integrals and fifth order expansions. Each of the three integral equations were solved independently using the appropriate HNC closure self consistently. The system of non-linear equations were numerically solved in real space using standard iterative Newton-Raphson techniques. The numerical accuracy for the multidimensional integrals was of the order of  $10^{-7}$  and they were calculated by using a 256 point Gaussian quadrature subroutine. The accuracy for solving the roots of the nonlinear equations was of the order of  $10^{-8}$ . The number of iterations needed for the integral equations to converge ranged from 45-123. In each case, global convergence was achieved to a tolerance level of  $10^{-6}$  for a change of the initial guess by 2 orders of magnitude.

As an accuracy check, the same RISM code was also used to study two systems unrelated to the present systems. The first test involved calculating the equilibrium solvation free energy as a function of reaction progress of the aqueous phase  $S_N2$  reaction of chloride with methyl chloride. As mentioned earlier in the introduction, the same calculations were performed earlier by Huston, Rossky and Zichi.<sup>25</sup> As such, the solute and solvent parameters were all obtained from the work of Huston et al.<sup>25</sup> The results of Ref. 25 were reproduced by our RISM code. A second test of the code was to calculate structural properties of NaCl in water. This work on alkali halides in water was originally performed by Pettitt and Rossky.<sup>36</sup> Again, Eqs.(4)-(6) were used to find the pair correlation functions for Na-O and Cl-O, as well as Na-H and Cl-H. The model used was the same as in Ref. 36. The radial distribution functions obtained from the present code were in agreement with those of Ref. 36.

### III. Application of RISM to Electron Transfer

#### A. Electron Transfer Model

The electron transfer model studied in this section consists of the  $Fe^{2+}/Fe^{3+}$  redox pair in water. For the most part, the model is the same as that used by Kuharski, *et al.*<sup>11</sup> At the reactant state, the charges of the ions were fixed at +2 and +3. At the transition state the charges on both of the ions were taken to be +2.5, consistent with the "tight binding" assumption that the electron density will resonate symmetrically between the  $Fe^{3+}$  cores.<sup>11</sup> The difference in the excess free energies between the two solvated solute charge distributions was taken to be the solvent activation free energy in this model.

The solvent in this model was the simple point charge (SPC) water model of Berendsen *et al.*<sup>44</sup> at a temperature of  $T = 298K$ , and an experimental number density at 1 atm of  $\rho = 0.03334 \text{ \AA}^{-3}$ . The total solvent pair potential in the SPC model consists of a long range site-site Coulomb term and a short range site-site Lennard-Jones term, i.e.,

$$-\beta u_{\alpha\gamma}^{vv}(\mathbf{r}) = -\beta u_{\alpha\gamma}^{*vv}(\mathbf{r}) + \phi_{\alpha\gamma}^{vv}(\mathbf{r}) \quad (9)$$

where the pair potentials for water have been decomposed in this notation. The short

range interactions are written as

$$u_{\alpha\gamma}^{*vv} = \left( \frac{C_{12}^{vv}}{r_{\alpha\gamma}^{12}} + \frac{C_6^{vv}}{r_{\alpha\gamma}^6} \right) \quad (10)$$

The coefficients for  $C_{12}^{vv}$  and  $C_6^{vv}$  are listed in Table I. In Eq. (9), the long range Coulomb terms are written as

$$\phi_{\alpha\gamma}^{vv} = -\beta \sum_{i,j} \frac{q_i q_j}{|\mathbf{r}_\alpha^i - \mathbf{r}_\gamma^j|} \quad (11)$$

where  $\mathbf{r}_i^i$  denotes the positions of atom  $i$  of molecule  $\alpha$  ( $i = \text{O}, \text{H}, \text{H}'$ ). The partial charges  $q_{\text{H}}$  and  $q_{\text{H}'}$  are equal to  $0.41e$  and  $q_{\text{O}} = -0.82e$  for oxygen, where  $-e$  is the charge of an electron. To avoid an unphysical overlap from occurring between the hydrogen and the oxygen atoms in RIS.  $\epsilon$  calculations, an alteration to the SPC model has been suggested by Pettitt and Rossky.<sup>35</sup> This alteration amounts to adding a repulsive term  $\epsilon(\sigma/r)^{12}$  to the O-H intermolecular site-site potential, where  $\epsilon = 0.8$  kcal/mol and  $\sigma = 1.6$  Å. This modification is required to ensure stability of the model since without it the total water-water pair potentials possess configurations with  $-\infty$  potential energy.

When solvated in water, both the ferric and ferrous ions are six-fold coordinated by water ligands. The symmetric  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  complex is octahedral, with the oxygen-ion bond lengths of approximately 2.0 Å. The oxygen-ion bond lengths are approximately 0.13 Å longer for the symmetric ferrous complex  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ . An effective ferric-water pair interaction was constructed by Kuharski *et al.*<sup>11</sup> that leads to the same structural behavior. This effective pair potential for the solute-solvent interaction is, as usual, divided into a short range interaction term

$$u_{\alpha\gamma}^{*uv} = \frac{A}{|\mathbf{r}_\alpha - \mathbf{r}_\gamma|^9} \quad (12)$$

where  $\mathbf{r}_\alpha$  is the position of the iron ion and  $A = 6392.7$  (kcal/mol)Å<sup>9</sup>, and the long range Coulombic interaction of the form

$$\phi_{\alpha\gamma}^{uv} = -\beta \sum_i \frac{3eq_i}{|\mathbf{r}_\alpha - \mathbf{r}_\gamma^i|} \quad (13)$$

Since the valence electron distribution in the  $\text{Fe}^{2+}$  ion is localized to a great degree, as noted earlier, one may estimate the  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  interaction from Eq. (13) by reducing the charge from  $3e$  to  $2e$ . That is, the  $\text{Fe}^{2+} - \text{H}_2\text{O}$  interaction is given by Eq. (13) with "3" replaced by "2".

For the solute-solute ( $u-u$ ) interactions, a Coulombic potential was used for the interionic terms. It is to be noted, however, that the corresponding intramolecular pair distribution function is always a delta function when the ions are held rigid. It is also important to note that one is rarely concerned with the solute-solute correlations *per se*, but rather in the solvent-mediated potential of mean force.

### *B. Results for Electron Transfer*

The RISM result for the activation energy in the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  electron transfer problem at a separation of  $6.075\text{\AA}$  was found to be 20.8 kcal/mol. This result is within 5% of the existing simulation result.<sup>11</sup> The number of oxygen atoms in the first solvation shell of each iron ion was calculated to be 6.2 at the transition state, which is consistent with simulation result<sup>11</sup> and known ligand coordination. In the reactant state, the number of first-shell oxygen atoms for the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions was 6.8 and 6.7, respectively. Figure 1 shows the  $\text{Fe}^{3+} - \text{O}$  and  $\text{Fe}^{2+} - \text{O}$  radial distribution functions from the RISM calculation, while Fig. 2 shows the corresponding potential of mean force between the two ions. Compared with Bader and Chandler's calculations,<sup>34</sup> Fig. 2 matches well with their results obtained using Ewald summations. The present results, however, do not agree with earlier RISM calculations of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  solvent activation free energy.<sup>31</sup> The reasons for this are unclear.

## **IV. Application of RISM to Proton Transfer**

### *A. Model Proton Transfer System*

This section describes the application of the extended RISM theory to a model intramolecular proton transfer reaction. In principle, this problem is similar to the electron transfer problem but for two important details. First, the ion distance is held rigid in the

electron transfer case, whereas the proton transfer complex is flexible. Thus, although the basic formalism will not change, the intramolecular direct and pair correlation functions of the proton transfer system will be different. Second, the solute has three sites with charges, rather than only two as in the electron transfer case.

The model proton transfer system consists of a three atom solute,  $[A \cdots H-A']^+$ , where A and A' atoms are the same species, and the complex is solvated in water.<sup>20</sup> The three RISM sites of the solute are the atoms A, A' and the proton. The proton is free to move between the  $A-H \cdots A'$  to the  $A \cdots H-A'$  configurations. The asymmetric stretch mode is taken to be the reaction coordinate. The solute-solvent, solute-solute and solvent-solvent interactions are summarized below. The RISM equations in Eqs. (4)–(6) were then solved with the HNC closure in Eq. (3) and the decomposition of the pair potentials in Eq. (9). The solvent activation free energy is defined as the difference in solvation free energy when the proton is in the reactant state to when the proton is at the transition state. As in the electron transfer problem, the solvent contribution to the excess free energy was found from Eq. (7).

The solvent in the proton transfer model was the simple point charge (SPC) water model at the same temperature and number density as before. For the solute-solvent interactions, the short range interactions between the atoms at sites A (and A') and the oxygen atoms of water were of the Lennard-Jones type, with the coefficients the same as that of O–O interactions in SPC water.<sup>44</sup> Analogous to the extra O–H repulsive term added in the solvent-solvent interactions, an additional repulsive term for the potential energy between A (and A') and the hydrogen atoms of the solvent was also added. The proton, A and A' atoms interact with the atomic sites on the water molecule by atom by Coulombic forces. The charge on the solute sites was determined by a charge switching procedure as a function of the solute asymmetric stretch coordinate.<sup>20</sup> The proton charge was held at a constant charge of  $+0.5e$ . The reactant and product charges varied under the constraint that the entire solute system should have a conserved charge of unity. The charges of the reactant and product sites were given by

$$e_A(q) = 0.25(1 - \tanh(q/q_{sw})) \quad (14)$$

$$e_{A'}(q) = 0.25(1 + \tanh(q/q_{sw})) \quad (15)$$

In the above equations,  $e_A$  and  $e_{A'}$  are the charges of A and A', respectively,  $q$  is the reactant coordinate, and  $q_{sw}$  equals 0.125 Å.

Unlike the electron transfer problem, the solute system was not a rigid system.<sup>20</sup> The potentials between the protons and the A atoms were Morse oscillators:

$$V_{A-H} = D[\exp(-2a(|\mathbf{r}_{AH}| - b)) - 2\exp(-a(|\mathbf{r}_{AH}| - b))] \quad (16)$$

In the above equation, the parameters were chosen to be  $D = 21.4$  kcal/mol,  $a = 5.4$  Å<sup>-1</sup>, and  $b = 0.95$  Å. The potential between the A and A' atoms was taken to be

$$V_{AA'} = (1/2)m_r\omega_{AA'}^2(\mathbf{r}_{AA'} - \mathbf{r}_{eq})^2 \quad (17)$$

where  $m_r = 20.0$  amu,  $\omega_{AA'} = 550$  cm<sup>-1</sup>, and  $r_{eq} = 2.5$  Å. A bending potential was also included to help maintain the linear configuration of the complex. This potential was of the form

$$V_{AHA'} = (1/2)\mu_r\omega_{bend}^2 r_0^2(\theta - \theta_{eq})^2 \quad (18)$$

where  $\theta_{eq} = 180^\circ$ ,  $\mu_r = 20.0$  amu,  $\omega_{bend} = 1000$  cm<sup>-1</sup>, and  $r_0 = 2.5$  Å.

### B. Results for Proton Transfer

The RISM result for the solvent activation free energy in the proton transfer problem was found to be 5.8 kcal/mol, while the simulation result is 4.4 kcal/mol. The latter result differs from that reported in Ref. 20 because 432 solvent molecules were used in the present case along with an improved Monte Carlo sampling algorithm. In addition, the repulsive interaction term that was added between the interaction sites A and A' and the hydrogen atoms in the RISM calculation was not included in simulations. Otherwise, the simulation was the same as in Ref. 20.

The disagreement between the RISM and simulation results is larger than in the electron transfer case, though the result is still reasonable. It should be noted that the

total solvent activation free energy is much smaller for the proton transfer than for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  electron transfer<sup>11</sup> or for the  $\text{S}_{\text{N}}2$  reaction<sup>25</sup> (i.e.,  $\sim 5$  versus  $\sim 20$  kcal/mol), so it is much easier to make a large relative error. Nevertheless, the subtleties of describing three-body charge transfer processes with RISM theory remain to be explored.

### V. Concluding Remarks

Extended RISM calculations of the solvent activation free energy for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  electron transfer system and a model proton transfer reaction have been presented. The agreement with simulation results in the electron transfer case was quite superior to the proton transfer case. The main differences between the electron and proton transfer model were the flexible, three site solute in the latter case along with a much lower solvent activation free energy. In general, it is perhaps fair to say that the present RISM results are mixed, but still rather encouraging. Future research will hopefully shed more light on the use of integral equations to predict solvent effects in condensed phase charge transfer reactions.

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**TABLE I.** Short-Range Potential Parameters<sup>a</sup> for SPC water.

$C_6^{(O-O)}$	$C_{12}^{(O-O)}$	$C_6^{(O-H)}$	$C_{12}^{(O-H)}$	$C_6^{(H-H)}$	$C_{12}^{(H-H)}$
-625.731	629624	0.000	225.180	0.000	0.000

<sup>a</sup>The units for  $C_6$  are in kcal Å<sup>6</sup>/mol and for  $C_{12}$  are in kcal Å<sup>12</sup>/mol.

### Figure Captions

**Figure 1:** Ferric-oxygen (solid line) and Ferrous-oxygen (dashed line) radial distribution functions from the RISM calculations.

**Figure 2:** Potential of mean force for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  system calculated from RISM theory.

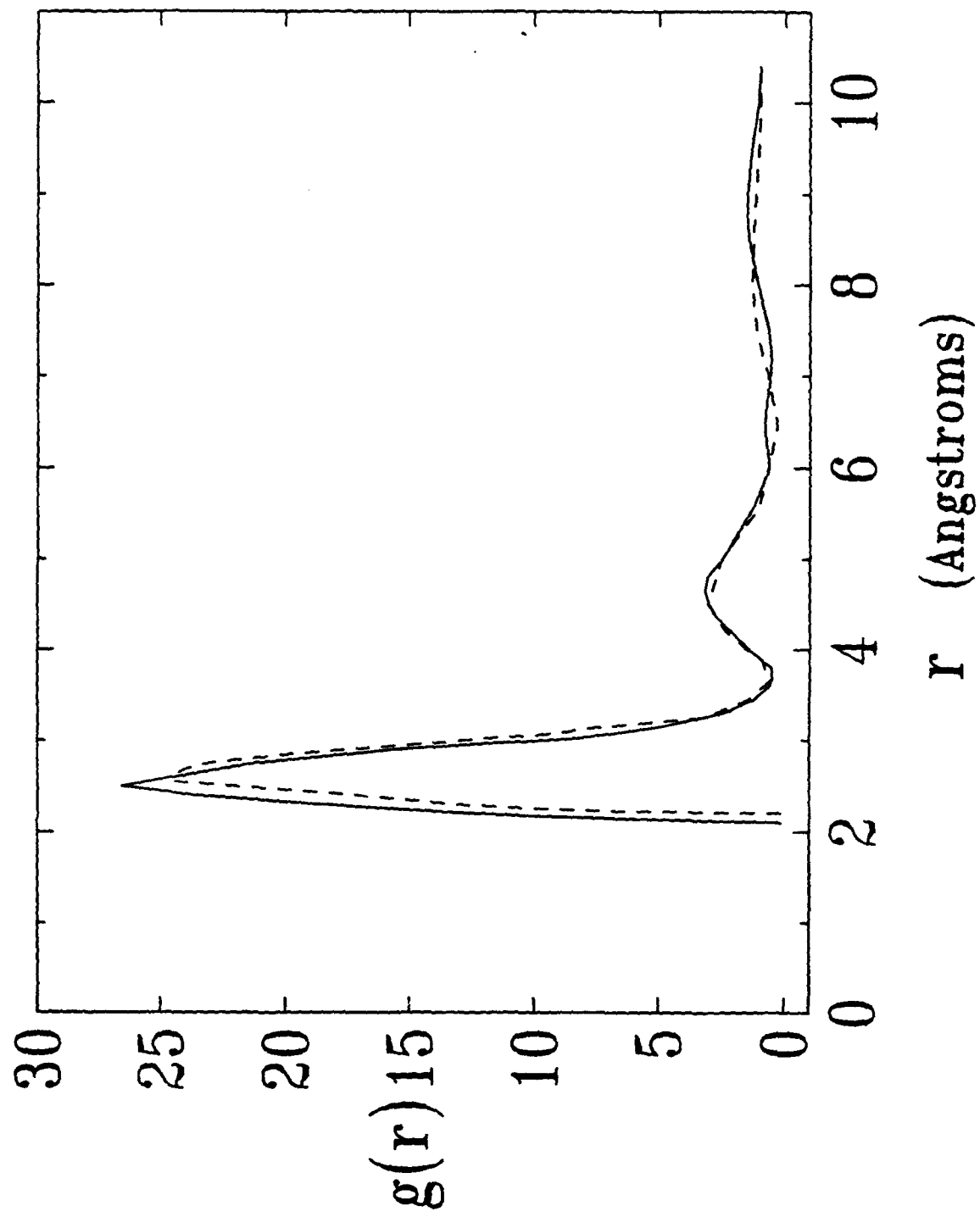


FIGURE 1

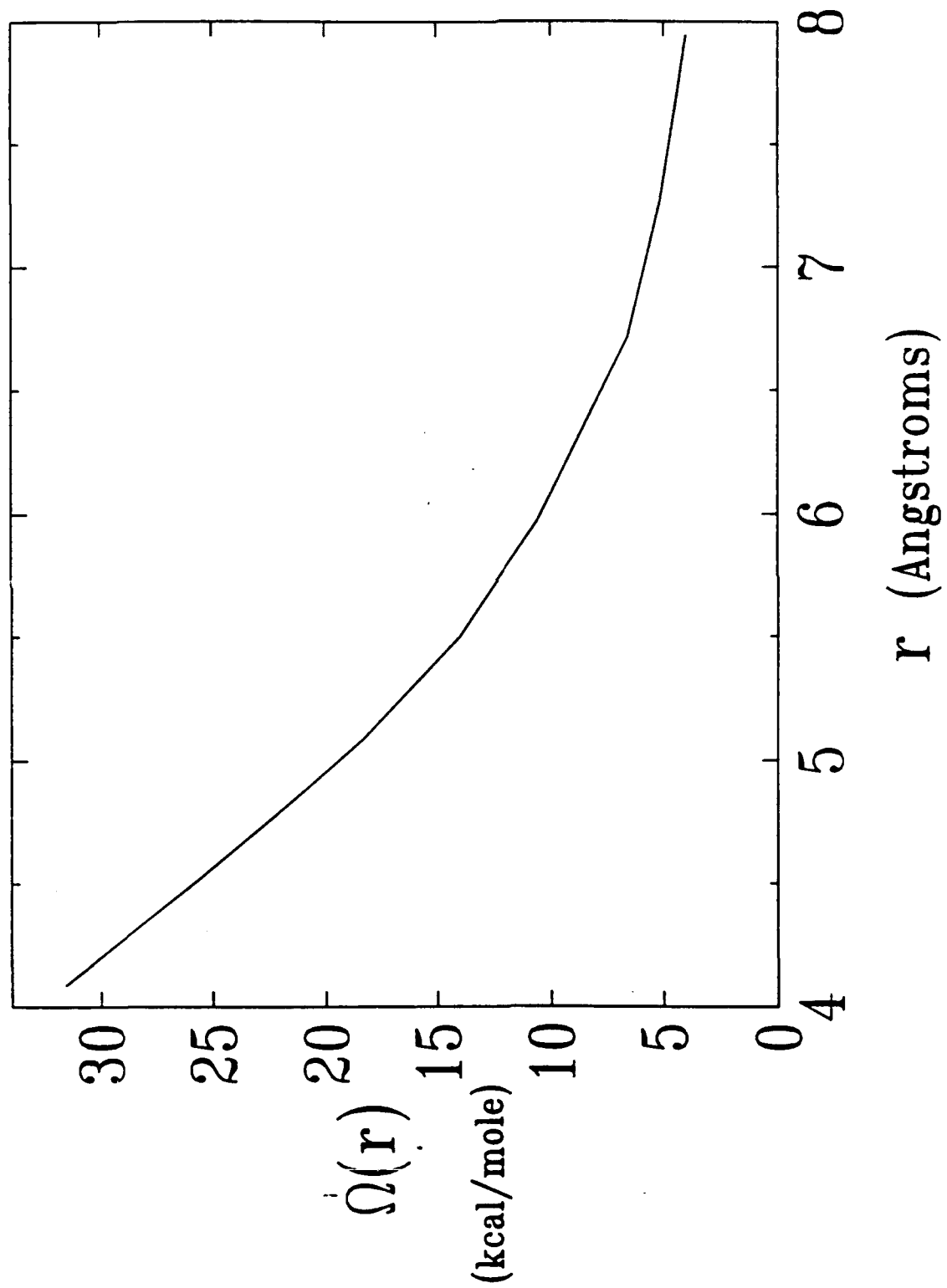


FIGURE 2